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CHEMICAL VAPOR DEPOSITED SILICA COATINGS FOR SOLAR MIRROR PROTECTION

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SUMMARY

A variety of techniques are available to apply protective coatings to oxidation susceptible spacecraft components, and each has associated advantages and disadvantages. Film application by means of chemical vapor deposition (CVD) has the advantage of being able to be applied conformally to objects of irregular shape. For this reason, a study was made of the oxygen plasma durability of thin film (less than 5000 Å) silicon dioxide coatings applied by CVD. In the present experiments, such coatings were applied to silver mirrors, which are strongly subject to oxidation, and which are proposed for use on the space station solar dynamic power system. The results indicate that such coatings can provide adequate protection without affecting the reflectance of the mirror. Scanning electron micrographs indicated that oxidation of the silver layer did occur at stress crack locations, but this did not affect the measured solar reflectances. Oxidation of the silver did not proceed beyond the immediate location of the crack. Such stress cracks did not occur in thinner silica films, and hence such films would be desirable for this application.

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INTRODUCTION

Early shuttle flights revealed that a number of materials commonly used in spacecraft and proposed for use on the NASA Space Station are subject to oxidation by the low-earth-orbit (LEO) atomic oxygen environment (ref. 1). One way to prevent oxidation of these materials is to apply an oxidation resistant, thin film coating. Such coatings can be applied by any of several techniques, including electron beam evaporation and ion beam or magnetron sputtering. Recent studies have shown the success of these coatings in the protection of both silver mirrors (refs. 2 and 3) and Kapton (ref. 4). An alternative means of applying such coatings is chemical vapor deposition (CVD). This technique has an important advantage in that it is not limited to line-of-sight deposition. Hence conformal coatings may be applied to objects of irregular geometry, which may make CVD useful in the application of protective coatings to other kinds of spacecraft components. For this reason, a study was undertaken to determine the effectiveness of CVD coatings for oxidation protection.

Highly reflective, lightweight, durable mirrors are required for the concentrator surfaces of the solar dynamic power module to be used on the space station. The last requirement is dictated by the presence of highly corrosive atomic oxygen at the space station orbital altitudes. For the reflecting surface, silver is the material of choice, because it offers the highest reflectance over the Air-Mass-Zero (AMO) solar spectrum. Since silver is highly susceptible to oxidation, a suitable protective coating is required. Previous work (refs. 2 and 3) to identify such coatings has shown that several materials are acceptable candidates. These include silicon dioxide, aluminum oxide, magnesium fluoride, and combinations of these.

For this study, silicon dioxide coatings were applied by CVD to silver mirror surfaces. Since silver surfaces are highly susceptible to oxidation, they provide an excellent means to test the oxidation protection afforded by these coatings. Also, the results can be compared to previous work in which coatings were applied by the other deposition techniques mentioned above.

APPARATUS AND PROCEDURE

Samples for evaluation consisted of 1000 Å of silver deposited onto polished nickel wafer substrates in an ion beam deposition system described elsewhere (ref. 5), followed by several different thicknesses of SiO_2 deposited by two different chemical vapor deposition techniques.

These techniques consisted of preparation under either atmospheric pressure or low (0.55 to 0.2 Torr) pressure conditions. In both cases, 99 percent pure tetraethoxysilane (TES) was used as the reagent. In the atmospheric pressure case, the TES was placed in a gas saturator and 300 SCCM of argon was passed through as the carrier gas. The deposition took place in an oven held at 675 °C. Deposition rates were on the order of 150 to 200 Å/min, and the resulting SiO_2 films exhibited a thickness uniformity of ±10 percent of the average value, as measured by ellipsometry.

In the low pressure case, no carrier gas was used, and the deposition took place in a tube furnace at 650 °C. Deposition rates were typically 60 Å/min and thickness uniformities were on the order of ±1 percent. Pressures were measured with an MKS Baratron capacitance manometer.

The LEO atomic oxygen environment was simulated using an SPI Plasma Prep II RF plasma reactor operated with ambient air as the carrier gas (ref. 6). For comparison purposes, 1 hr of exposure in this reactor is equivalent to 1×10^{19} atoms/cm^2 equivalent fluence as measured by Kapton erosion from early shuttle flights. For Kapton, 26 hr of exposure in the reactor produces erosion equivalent to 1 year exposure in space. Reflectance measurements were made with a Perkin-Elmer Lambda-9 UV/VIS/NIR spectrophotometer equipped with a 60-mm diameter integrating sphere. The operation of this instrument and the calculation of the integrated solar reflectances reported here are described elsewhere (ref. 2). Specular reflectance values are for a 0.1 steradian solid angle. Measured reflectances carried an uncertainty of ±1 percentage point.

After preparation, the solar reflectance of each sample was measured prior to and then at regular intervals during plasma exposure. Several of the samples were subsequently examined with scanning electron microscopy.

RESULTS AND DISCUSSION

Figure 1 presents the effect of the RF plasma environment on the various samples prepared for this study. Overall, no significant effects of the plasma environment on reflectance durability were noted for any of the samples. Each appeared adequate to protect a silver surface from oxidation. Differences were noted, however, in terms of absolute reflectance, visual appearance, and appearance under SEM.

Atmospheric Pressure CVD

In visual appearance among the atmospheric pressure CVD samples, the 2000 Å SiO_2 sample fared better than the thicker ones (4000 to 4700 Å) during plasma exposure. The thicker samples showed a significant degree of cracking, principally along one axis. The 2000 Å sample showed no cracking. The cracks were apparent even before plasma exposure; however the degree of cracking increased somewhat during exposure (≈5 percent).

Examination of the two thicker samples under scanning electron microscopy revealed that, in most instances, the cracks extended down to the silver layer. Figure 2 shows a typical region of the surface of the sample with the 4700 Å thick SiO_2 coating. At most locations along the cracks, silver oxide can be seen protruding through the coating. Figure 3 is an enlargement of a portion of figure 2, and clearly shows the protruding oxide. The growth of this oxide, however, did not have an effect on specular reflectance, which indicates that the surface area of the cracks was small compared to the total sample surface area. Also visible is evidence of multiple fractures along a crack line. These fractures suggest that the cracks are a result of compressive stresses in the film which arise from the greater degree of contraction of the nickel substrate relative to the coating after the heating occurring during deposition. This can also explain the slightly increased degree of cracking observed during plasma exposure mentioned above. As a side effect, the samples are heated to approximately 60 °C during oxygen plasma exposure, and the continual heating and cooling from repeated exposures continues to stress cycle the film and results in additional cracks. No evidence is seen, however, of any undercutting of the protective coating by the oxygen plasma. This would have been expected to appear as a front of discoloration surrounding the crack edges, which is behavior seen previously (ref. 6) on protected silver layers on non-oxidizable substrates. The previous work suggested that the oxidation process would eventually cease, due to the inability of the oxygen atoms to diffuse through the silver oxide to reach fresh, unoxidized silver. This appears to be the case here.

As with the 4700 Å coating, the 4000 Å SiO_2 coating showed a significant degree of stress cracking. Figure 4 is an SEM photo of one of these fissures and, similar to figure 3, shows a high degree of local "shattering" of the coating. At the location of figure 4, however, no oxidation of silver is evident, indicating that the crack did not extend to the silver layer. This is not true in figure 5, which is an SEM photo of a different location on the surface of the sample in figure 4. Here a significant degree of oxidation along a crack can be seen.

In comparison with the SiO_2/Ag/nickel substrate samples described in reference 2, the atmospheric pressure samples prepared here exhibited nearly identical solar reflectance values. All were in the 90 percent range.

Low Pressure CVD

As stated above, the reflectance of the low pressure CVD sample (2000 Å of SiO_2) also was unaffected by the oxygen plasma. Overall, however, the absolute reflectance of this sample was considerably lower (10 to 15 percent) than that of the atmospheric pressure CVD samples. No stress cracks were noted in this sample; however, on the whole the sample had a somewhat cloudy white appearance, which accounts for the lower reflectance. The cause of this was not known, and needs to be investigated.

CONCLUSIONS

Silica coatings prepared by atmospheric pressure and low pressure chemical vapor deposition techniques are suitable for use as protective coatings on solar mirrors. The silver layer was protected from the laboratory oxygen plasma environment, and measured reflectances were as high as has been measured for protective-coating/reflector systems prepared by other techniques. The problem of cracking can be addressed by use of a thinner layer of SiO_2, and could possibly be reduced or eliminated if a substrate were used whose coefficient of thermal expansion more closely matched that of silica.

Use of CVD for oxidation resistant protective coatings would not be limited to protection of silver mirrors. One of the great advantages of CVD is that the deposition process is not line-of-sight and hence there exists the ability to coat objects of widely varying sizes and shapes with coatings of uniform thickness. Such an ability would be of great utility in atomic oxygen protection of other low-earth-orbit spacecraft components, such as truss and boom support structures, and textured radiator surfaces. The disadvantage of CVD is the requirement that the object being coated be heated, which may preclude its use in applications where the substrate has a low melting point or would be otherwise adversely affected by heat.

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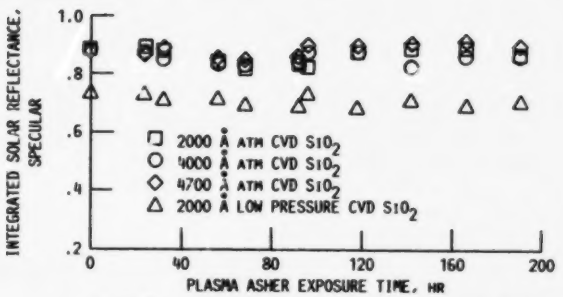

FIGURE 1. SOLAR SPECULAR REFLECTANCE VERSUS OXYGEN PLASMA EXPOSURE TIME FOR THE REFLECTOR SAMPLES (VARIOUS THICKNESSES OF SiO_2 ON 1800 Å OF SILVER ON NICKEL SUBSTRATES) PREPARED IN THIS STUDY.

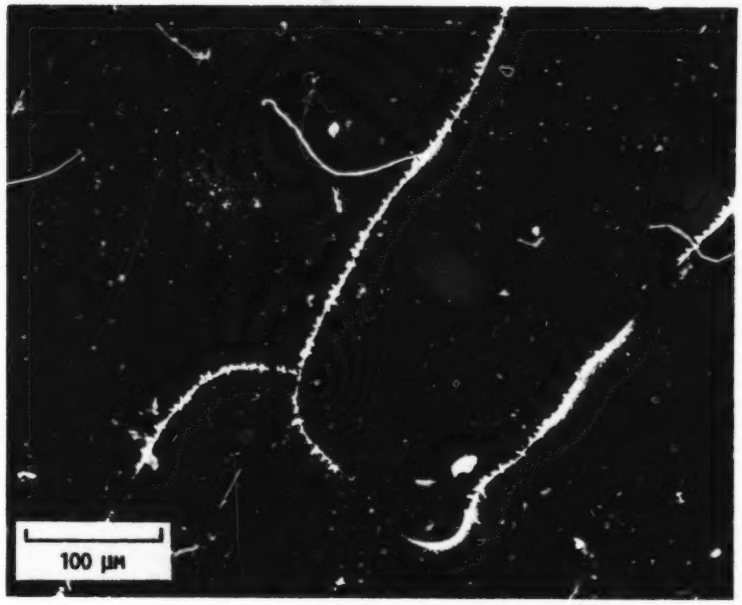

FIGURE 2. - EXAMPLE OF CRACKING OBSERVED ON SAMPLES WITH THICKER (4700 Å) SiO_2 COATINGS. PROTRUSION OF SILVER OXIDE THROUGH CRACKS IS EVIDENT. RF PLASMA EXPOSURE TIME WAS 190 HR.

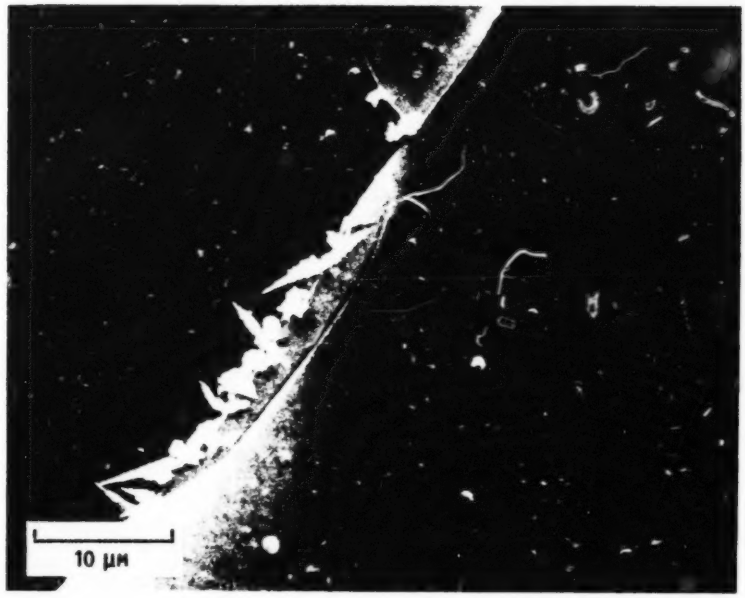

FIGURE 3. - DIFFERENT REGION OF SAME SAMPLE SHOWN IN FIG. 2, BUT AT HIGHER MAGNIFICATION. MULTIPLE FRACTURES ALONG THE CRACK INDICATE STRESS DUE TO DIFFERENT COEFFICIENTS OF THERMAL EXPANSION BETWEEN THE SUBSTRATE AND COATING.

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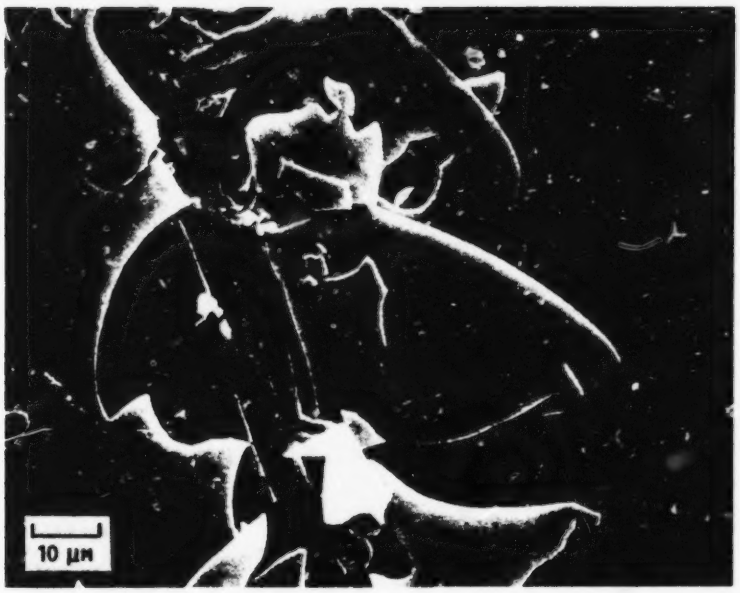

FIGURE 4. - AN EXAMPLE OF A CRACK WHICH DID NOT PENETRATE THROUGH TO THE SILVER LAYER, AS EVIDENCED BY ABSENCE OF SILVER OXIDE. SiO_2 COATING WAS 4000 Å THICK. RF PLASMA EXPOSURE TIME WAS 190 HR.

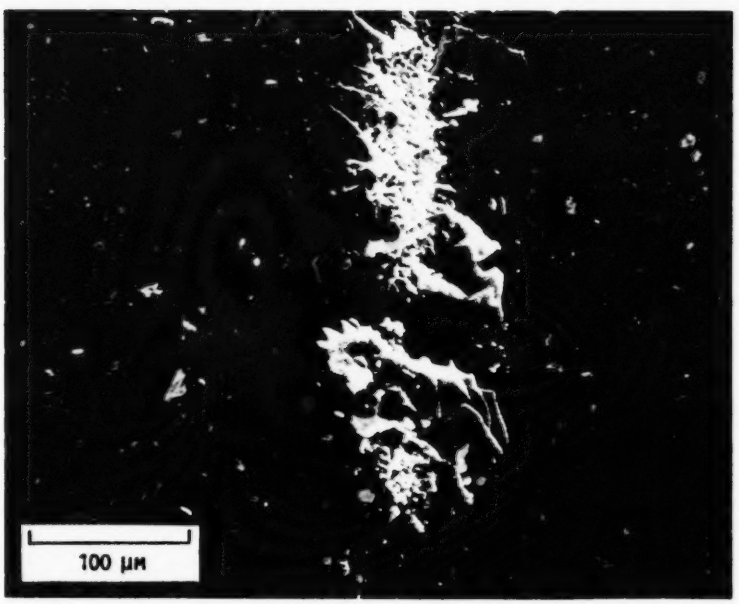

FIGURE 5. - DIFFERENT REGION OF SAME SAMPLE SHOWN IN FIG. 4 SHOWING A CRACK WHICH DID PENETRATE THROUGH TO SILVER LAYER.

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16. Abstract

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